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SIMULATED PRECIPITATION REFERENCE MATERIALS

J. K. Taylor, et al

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The preparation of a series of reference materials for chemical analysis of natural precipitation is described. The materials consist of ampoules of concentrates which can be diluted to simulate naturally collected samples of rainwater. The analytical measurements made to verify the composition of the samples are also described.

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Simulated Precipitation Reference Materials

John K. Taylor, E. R. Deardorff, R. A. Durst,
E. J. Maienthal, T. C. Rains, and E. P. Scheide

ABSTRACT

The preparation of a series of reference materials for chemical analysis of natural precipitation is described. The materials consist of ampoules of concentrates which can be diluted to simulate naturally collected samples of rainwater. The analytical measurements made to verify the composition of the samples are also described.

KEY WORDS

Chemical analysis; rainwater analysis; reference materials.

1. INTRODUCTION

This report describes work done at the National Bureau of Standards to prepare reference materials needed for the evaluation of methodology and for the verification of data concerned with the analysis of rainwater and other forms of precipitation. Such measurements can provide valuable information on global pollution levels, atmospheric circulation, and geophysical phenomena when the data are validated. However, the reliability of such measurements is presently unknown.

In recognition of this situation, the National Bureau of Standards has investigated the problems of producing synthetic aqueous concentrates which simulate natural precipitation samples when quantitatively diluted.

The work reported here was initiated at the request of and supported by the Environmental Protection Agency under an Interagency Agreement and resulted in the preparation and analysis of a series of four concentrates of graded composition, and two additional sets of "unknowns" within the compositional range.

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2. EXPERIMENTAL DETAILS

2.1 General Considerations

A decision was made to produce four concentrates which could be diluted to simulate natural precipitation samples. The reference materials would consist of 10 ml of appropriate solutions, sealed in ampoules, which would be quantitatively diluted to a final volume of 500 ml by the user. The four concentration levels were chosen to represent the range of composition of samples ordinarily encountered in rainwater analysis.

The constituents and compositional levels recommended by EPA are given in table 1. However, some compromises had to be made in preparing the reference samples. From materials balance considerations, it was evident that there were missing constituents. There were also problems concerned with achieving specified values for gross parameters such as pH, conductivity, and acidity when chemical constituents are specified.

A further problem is concerned with the actual synthesis of the samples. Natural processes cannot be duplicated in the laboratory. Hence, incompatibilities can occur during mixing of constituents which would not occur under natural conditions.

The recommended compositions were found to be deficient in anions. This could be rectified by addition of other anions but this would disturb the cation balance and also could conceivably cause compatibility problems. Furthermore, the basis for choice of the balancing anion was not clear. Accordingly, it was decided to use the values in table 1 as guidelines and to prepare the reference samples with the cationic constituents as the major consideration. The anionic constituents would approach the recommended levels as far as possible. The gross parameters would be permitted to assume values consistent with this approach.

A further complication is that of compatibility of constituents which is influenced by the order, rate of addition, and concentration of the individual constituents at time of addition to the bulk solution. The fact that the reference samples were to be 50 times more concentrated than the final solutions also complicated this problem, since compatibility needs to be achieved for the concentrates.

2.2 Preparation of Reference Materials

In consideration of the problems outlined in Section 2.1, compromise concentration levels were adopted and experimental work was undertaken to investigate their feasibility. During this work, two problems were identified It was found difficult to retain iron at anywhere near the recommended level, so it was eliminated. Also there was some precipitation of lead in the most concentrated solution. Since this did not appear to be a major problem, it was decided to tolerate it, but to filter the solution before ampouling.

The chemicals used to prepare the reference materials are listed in table 2. In general, they were reagent grade chemicals and were believed to be of sufficient purity to permit calculation of the amount of constituent added without assaying them. However, it was later found that several of the hydrated salts were not the nominal compositions. Trace impurities in the chemicals are of no significance for the present situation. The selection of the chemicals was somewhat arbitrary to attain the desired anionic and cationic compositions. Laboratory grade distilled water was used for dilution purposes.

The amounts of chemicals used to prepare the bulk solutions are given in tables 3, 4, 5, and 6. For Solutions A, C, and D, half of the constituents were added to approximately 2 l of water in a volumetric flask and then diluted to the mark. A second solution was prepared containing the remaining constituents. These solutions were combined and the resulting solution was filtered through a quantitative paper (S & S 589 Blue Ribbon)*. In the case of Solution B, an additional volume of 2 l of distilled water was added before filtering. The final solutions were stored in pyrex bottles of appropriate size prior to ampouling. No visible precipitation occurred during the storage period which was about 30 days.

2.3 Ampouling

The bulk solutions were transferred to ampoules using the automatic dispensing and sealing equipment of the Office of Standard Reference Materials. The ampoules used (Wheaton Cat. No. 176780) are made from borosilicate glass formulated to prevent a change of pH and to maintain the purity of the contents. They are pre-scored to eliminate the need for filing.

*Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

The dispensing equipment pumps the solution from the storage vessel and reproducibility injects a pre-set volume into the ampoules. Ampoules randomly selected for analysis were also weighed to verify the reproducibility of the filling operation. No significant changes were detected during the entire filling operation for the four solutions, which was done during a three-hour period.

The dispensing equipment automatically flame-sealed the ampoules. These were then placed in their original shipping boxes, in the order of filling.

2.4 Numbering Sequence

The ampoules were labeled and numbered in the following sequences:

Solution A – 75001A to 75320A
Solution B – 75001B to 75520B
Solution C – 75001C to 75320C
Solution D – 75001D to 75320D

Twenty samples were randomly selected from each lot for chemical analysis. The remainder of the ampoules were delivered to EPA.

In addition to the ampoules noted above, additional ampoules amounting to approximately 40 in each lot were filled, depending upon the amount of solution available. These ampoules were also numbered in a continuation of the same sequences and will be retained at NBS for further study.

2.5 Analysis of Bulk Solutions

The bulk solutions were analyzed for their cationic constituents by atomic absorbtion and flame emission spectrometry. The results, reported in tables 7 to 10 indicate that the desired concentration levels had been acheived, except in the case of lead in Solution D where it was known that some initial precipitation had occurred. The data are also useful to evaluate any long-term deterioration of the samples, either by loss or leaching processes.

2.6 Analysis of Ampoules

Twenty ampoules randomly selected from each lot, and additional ampoules randomly selected from the excess of the lots were analyzed as will be described in the following sections. The analysts also weighed the ampoules before and after delivery of their contents to evaluate the reproducibility of the filling operation.

2.6.1 pH Measurements

The pH measurements were made on diluted samples of the concentrate (1 ml sample + 49 ml H_2O). The combination pH electrode was calibrated with pH 4.01 and 7.00 buffers and the sample pH readings were taken directly from the digital pH meter display. Since the water used for diluting the samples was in approximate equilibrium with ambient CO_2, the values found for the pH were consistent with what would be expected for air-equilibrated water, i.e., pH 5.6 to 6.0, and indicate that there is little acid-base character to the samples themselves.

2.6.2 Conductivity Measurements

The conductivity measurements were made on the same diluted samples as the pH determinations. The cell constant, k, was determined using 0.01 M and 0.001 M KCl solutions having specific conductances, L, of 0.00141 and 0.000147 $S \cdot cm^{-1}$. The specific conductance of the sample solutions was calculated from the measured resistance at a frequency of 1 kHz by the equation:

$$L = \frac{k}{R} = \frac{0.0307\ cm^{-1}}{R}$$

2.6.3 Acidity Measurements

Measurement of acidity was made by the method described in the EPA Manual of Methods for Chemical Analysis of Water and Wastes. The pH of a 10 ml sample was measured followed by addition of standardized sulfuric acid to pH 4. Hydrogen peroxide (30%) was added and the solution was boiled for several minutes. After cooling, it was titrated with standardized sodium hydroxide to pH 8.2 and the acidity was calculated as mg/liter $CaCO_3$.

Measurements were made on the concentrates to obtain increased precision and also on the reconstituted rainwater in the case of Solution D. The latter measurements were consistent with calculations based on a 50 fold dilution of the concentrate. The values reported in tables 7-10 are calculated for the reconstituted sample on the basis of a 50 fold dilution of the concentrate.

2.6.4 Analysis for Anions

2.6.4.1 Measurements for Sulfate Ion

The sulfate determinations were accomplished by titration with lead nitrate solution using the lead ion-selective electrode as the end-point detector. The indirect determination of sulfate is based on the formation of $PbSO_4$ which is quantified by measurements with a lead electrode. The measurements were carried out in 80 percent by volume isopropanol using a double-junction reference electrode. The sulfate analyses were performed using a Gran plot of the titration standards of known amounts of sulfate with standard lead nitrate. These were compared to the unknown samples. The Gran plot technique permits titration measurements to be taken beyond the equivalence point where Pb^{++} is in excess and the electrode responds optimally. It also results in a linear extrapolation to the end-point which simplifies the data interpretation. Before each sulfate determination, a blank was run to check the electrode response and to determine the blank correction. Also, the electrode was repolished after each sample was run to remove surface contamination. Without re-polishing, the electrode response becomes progressively slower and non-ideal. The concentrates were initially diluted, if necessary, to a sulfate concentration of approximately 10^{-5}M. Two milliliters of these were diluted with 8 ml of isopropanol prior to titration. Triplicate analyses were done on each sample and standard.

2.6.4.2 Measurements for Nitrate

Measurements for nitrate were made by the Brucine Method following the procedure in ASTM Method D 992-71, Nitrate Ion in Water. Nitrate ion reacts with brucine in strong sulfuric acid to develop a yellow color. A calibration curve was made with pure potassium nitrate to obtain a smooth curve in the range 0 to 250 µg/25 ml where the solution does not follow Beer's Law. The absorbance was read at 410 nm, using 1 cm cells. A sample size of 5 ml was used in these measurements.

2.6.4.3 Measurement of Fluoride Ion

The fluoride determinations were performed by direct potentiometry on ampoule samples diluted 1:2 with TISAB (total ionic strength adjustment buffer). Calibration standards containing 2, 20, and 100 ppm F^- were also prepared by 1:2 dilution with TISAB to permit direct reading of the sample fluoride concentrations. The electrode response was Nernstian over this range and the emf readings on both samples and standards were generally stable.

2.6.4.4 Measurement of Chloride Ion

Two analytical techniques were used to determine the chloride content of these samples. For the higher concentrations (samples "C", "D"), an automatic chloride titrator was used. This method is based on the amperometric generation of silver ions in situ which is automatically stopped at the end point by a potentiometric detector. Duplicate, and sometimes triplicate, 100-µl samples were used and the reproducibility between duplicates was generally better than 1 percent. The chloride titrator was calibrated with 500 and 1000 ppm standards.

Samples "A" and "B" did not contain sufficient chloride to activate the potentiometric sensor in the titrator, and it was necessary to determine the chloride in these samples by direct potentiometry using a chloride ion-selective electrode. Calibration standards containing 1, 10, and 100 ppm were used and, over the sample concentration range, the response was linear and approximatly Nernstian (54.2 mV/pCl). The precision of these measurements was not good, being about ±5 percent for the "B" samples and ±10 percent for the "A" samples. It is assumed that the observed deviations are due to measurement imprecision rather than actual differences between ampoules.

2.6.5 Analysis for Cations

2.6.5.1 Measurement of Ammonium Ion

Measurement for ammonium ion were made by two methods. An ammonia electrode was used to determine ion concentration by direct potentiometry. The sample and standard solutions (2, 20, and 200 ppm) were diluted 1:2 with 1.0 M NaOH to convert all of the NH_4^+ to NH_3 which is measured by the electrode. Although the electrode response over the concentration range of interest was good (55.5 mV/pNH_3), there was excessive electrode drift during the measurements, possibly due to the difficulty in measuring a volatile component in a very small volume of solution. As a result, little confidence was ascribed to the data.

The second technique consisted of chemical measurement according to the procedure given in the following reference: C. O. Willits and C. L. Ogg, "1949 Report of Standardization of Microchemical Methods, Micro Kjeldahl Nitrogen Determinations," USDA Eastern Regional Research Laboratory, Philadelphia, PA. A micro-Kjeldahl steam distillation apparatus was used to separate the ammonia released by sodium hydroxide, which was trapped in boric acid. The ammonia was titrated with standardized 0.01 N hydrochloric acid using methyl purple indicator. Both 5 ml and 10 ml samples were used for these measurements.

Because of the problems which were encountered in the analysis using the ion-selective electrode, the values obtained using this method were used only for evaluation of homogeneity. Accordingly, the values reported in tables 7 to 10 are based on the second method only.

2.6.5.2 Metals by Atomic Absorption and Flame Emission Spectrometry

All of the metallic cations were measured by atomic absorption or flame emission spectrometry. Measurements were made both on the bulk solution and on the ampoules. The contents of an ampoule were quantitatively transferred to a 100 ml volumetric flask. After addition of 1 ml of purified nitric acid, the solution was diluted to the calibrated volume. Emission or absorption measurements were made in duplicate. Calibration standards were made by dissolution of pure salts or pure metals.

2.6.5.3 Metals by Polarographic Analysis

Polarographic measurements were made for selected elements, on reconstituted samples, i.e. a solution resulting from dilution of the contents of an ampoule to a final volume of 500 ml.

Measurements of copper, lead, cadmium, nickel and zinc were made on the diluted samples in the following manner. Aliquots of 100 ml of the diluted samples were evaporated to dryness in quartz beakers, after addition of a few drops of perchloric acid. After a second evaporation with hydrochloric acid, the residues were redissolved in 2 ml of supporting electrolyte. For the case of copper, lead, and cadmium, the supporting electrolyte was ammonium acetate - acetic acid. A supporting electrolyte of pyridine - pyridinium sulfate was used for measurement of nickel and zinc. Measurements were made with a cathode-ray polarograph. Calibration standards and blanks were carried through the procedure.

Additional ampoules were analyzed similarly, except they were also rinsed with nitric acid and these rinsings were included in the analysis.

3. ANALYTICAL RESULTS

The analytical results obtained for the four reference materials are summarized in tables 7, 8, 9, and 10. These include data for the bulk solutions, analysis of individual ampoules, and measurements on the reconstituted solutions in several cases. However, all data are reported on the basis of the reconstituted solutions (dilution of 10 ml to a final volume of 500 ml). The columns labelled "Synthesis" contain values calculated from the composition of the solutions as prepared.

The last column of each table lists the recommended values for each parameter based on a "best estimate" in consideration of the synthesis values and the analytical limits of uncertainty. When the two values are in essential agreement, the synthesis values are recommended. This is the case for most of the parameters. The analytic values are recommended in several cases where uncertainties in the compositions of the starting materials, or loss or gain of a constituent was found or believed to be a reasonable explanation of the discrepancy.

All of the cadmium values are larger than expected. In view of the good agreement between the two measurement techniques, the discrepancy is believed to be due to non-stoichiometery of the hydrates used for preparation of the solutions, hence the measured values are recommended. The values found by polarographic measurement of copper in the reconstituted solutions are slightly smaller than expected. Since the synthesis values were found for solutions resulting from rinsing the ampoules with acid, it is concluded that a small loss of copper has resulted from interaction with the ampoules. Because acid rinsing is not permissible, the measured values are recommended. The values found for lead by two techniques are also lower than expected. Again, values in agreement with the bulk solution were found for ampoules rinsed with acid. Accordingly, it is concluded that losses have occurred as the result of interaction with the ampoule walls, so the measured values are again recommended.

The values found for calcium in samples B and D are somewhat lower than expected but agreement was found in the case of samples A and C. In view of this latter agreement and the confidence in the analytical procedure, the measured values are recommended for solutions B and D.

The measured values for fluoride are low by a few percent for all solutions except A although the differences are barely significant. However, in view of the care exercised in making the measurements, it is believed that the measured values are more likely and they are recommended for these solutions.

The only other significant departure from the expected values is that for sulfate in solution B. When the discrepancy was noticed, the measurement was repeated to verify the analytical value which is recommended.

It is not possible to assign uncertainty limits to the recommended values, because of limited experience with these materials. In most cases, the analytical measurements were

made with techniques used at NBS that are capable of providing data reliable to within 2 percent. However, stability problems may be an overriding factor of unknown magnitude. The best statement that can be made at present is that the data are believed to be useful to two significant figures.

4. DISCUSSION

The suitability of the samples to serve as reference materials or for intercalibration of measurement laboratories is based upon several types of information. Each ampoule contains the same weight of solution within close limits. Weighing of eighty ampoules indicated an average weight content of 9.963 g with a standard deviation of 0.005 g. Accordingly, it is clear that variations in the total amount of the contents are of no concern.

Measurements on replicate ampoules in each series were also made for most of the parameters to obtain information on possible variation between samples. These ranged from duplicates for 2 parameters to septuplicates on 9 parameters. No variations larger than the expected measurement variations were found. Accordingly, it is believed that all of the samples in a given series are reasonably identical in composition.

Because the materials consist of filtered solutions, uniformity of composition between ampoules would be expected, provided the contents are stable. It would have been preferred to study the stability over an extended period of time but the time schedule did not permit this. Accordingly, the long-term stability has not been established.

A few minor stability problems are evident from inspection of the data in tables 7 to 10. The values for sodium appear to be increasing, perhaps due to leaching from the walls of the ampoules. The values for copper and lead appear to have decreased since ampouling. It was found that the loss can be regained by an acid wash but this is not a permissible operation. However, the samples appear to be satisfactory for collaborative studies, especially if all measurements are carried out within a reasonably comparable period of time.

Samples have been retained by NBS and these will be analyzed after a suitable period of time to further evaluate their stability.

5. RECOMMENDED DILUTION PROCEDURE

The samples consist of ampoules of concentrate which simulate rainwater, when diluted to 500 ml. The ampoules are pre-scored at the constriction to facilitate breaking off the tip. Glassware should be thoroughly cleaned and rinsed with distilled water before use. The distilled water used for rinsing and dilution should be of the highest quality since any impurity will add to the constituents of the sample. The recommended procedure for preparation of the test sample is as follows:

1. Rinse the outside of the ampoule to remove dust and allow to air dry.

2. Hold ampoule in a vertical position, tip up, and gently tap to transfer any liquid from the tip to the body of the ampoule.

3. Hold ampoule with a paper towel (precaution to prevent injury to hand) and snap off the tip at the scored constriction.

4. Place a clean funnel in the neck of a clean 500 ml volumetric flask and transfer the contents of the ampoule, with gently shaking as required to facilitate removal of liquid.

5. Rinse the ampoule two times with distilled water and transfer the rinsings to the flask.

6. Add distilled water to the flask to dilute to the graduation mark, and mix contents thoroughly.

7. Treat the resulting solution with the same care and in the same manner as a sample of natural rainwater.

6. ACKNOWLEDGEMENTS

This work was done under the general supervision of John K. Taylor. Mr. Erle R. Deardorff prepared the solutions and performed analyses for nitrate, ammonia, and acidity. Mr. T. C. Rains and Ms. M. A. Waguespack performed the atomic absorbtion and flame emission measurements. Dr. R. A. Durst made the measurements of pH, conductance, and analyses for fluoride, chloride, and ammonium by the ion-selective electrode. Dr. E. P. Scheide anlyzed the samples for sulfate ion. Ms. E. J. Maienthal made polarographic measurements on the diluates for five metals. Mr. W. P. Reed of the NBS Office of Standard Reference Materials was responsible for the ampouling of the samples.

Table 1. Proposed Reference Standards

Sample	A	B	C	D
Constituent (unit of measurement)	Value	Value	Value	Value
pH	5.70	4.90	4.50	4.00
Conductivity (μScm^{-1})	35.0	50.0	65.0	90.0
Acidity (μeq)	.1	1.0	5.0	10.0
$SO_4^{=}$ (S)[1] (mg/l)	1.0	3.0	5.0	10.0
NO_3^- (N)[2] (mg/l)	.1	1.0	5.0	10.0
NH_4^+ (N)[2] (mg/l)	.1	1.0	5.0	10.0
F^- (mg/l)	.1	.1	.2	.3
Cl^- (mg/l)	.1	1.0	5.0	10.0
Na^+ (mg/l)	.1	1.0	5.0	10.0
K^+ (mg/l)	.05	.1	1.0	5.0
Ca^{++} (mg/l)	.1	1.0	5.0	10.0
Mg^{++} (mg/l)	.05	1.0	5.0	10.0
Zn^{++} (mg/l)	.02	.1	.3	.6
Cd^{++} (mg/l)	.03	.1	.5	1.0
Cu^{++} (mg/l)	.05	.1	.2	.4
Ni^{++} (mg/l)	.02	.1	.5	1.0
Fe (mg/l)	.05	.1	.2	.5
Pb^{++} (mg/l)	.02	.1	.2	.3
Mn^{++} (mg/l)	.05	.08	.1	.2

Table 2. Chemicals Used for Preparation of Reference Solutions

Chemical	Formula	Source
Calcium Chloride	$CaCl_2 \cdot 2H_2O$	Mallinckrodt Analytical Reagent
Calcium Sulfate	$CaSO_4$	Hammond Drierite Company
Magnesium Chloride	$MgCl_2 \cdot 6H_2O$	Mallinckrodt Analytical Reagent
Magnesium Sulfate	$MgSO_4$	B & A Reagent
Zinc Chloride	$ZnCl_2$	Fisher Certified
Zinc Nitrate	$Zn(NO_3)_2 \cdot 6H_2O$	Baker Analyzed
Cadmium Chloride	$CdCl_2 \cdot 2\frac{1}{2}H_2O$	Baker Analyzed
Cadmium Nitrate	$Cd(NO_3)_2 . 4H_2O$	Fisher Certified
Cupric Chloride	$CuCl_2 \cdot 2H_2O$	Fisher Certified
Cupric Nitrate	$Cu(NO_3)_2 \cdot 3H_2O$	Baker Analyzed
Cupric Sulfate	$CuSO_4 \cdot 5H_2O$	Fisher Certified
Nickel Nitrate	$Ni(NO_3)_2 \cdot 6H_2O$	Mallinckrodt Analytical Reagent
Nickelous Sulfate	$NiSO_4 \cdot 6H_2O$	B & A Reagent
Lead Nitrate	$Pb(NO_3)_2$	Baker Analyzed
Manganese Chloride	$MnCl_2 \cdot 4H_2O$	Mallinckrodt Analytical Reagent
Ammonium Chloride	NH_4Cl	Baker Analyzed
Ammonium Sulfate	$(NH_4)_2SO_4$	Mallinckrodt Analytical Reagent
Sodium Fluoride	NaF	Fisher Certified
Sodium Nitrate	$NaNO_3$	Baker Analyzed
Sodium Sulfate	Na_2SO_4	Mallinckrodt Analytical Reagent
Potassium Chloride	KCl	Fisher Certified
Potassium Nitrate	KNO_3	Baker Analyzed
Potassium Sulfate	K_2SO_4	Fisher Certified

Table 3. Chemicals Used to Prepare Solution A
(Weight in mg to prepare 4 liters)

	mg	mg $SO_4^{=}$	mg NO_3^-	mg F^-	mg Cl^-	mg Reagent
Ca^{++}	19.77	47.38				67.15
Mg^{++}	20.83	82.32				103.15
Zn^{++}	4.25				4.60	8.85
Cd^{++}	5.18				3.27	10.53
Cu^{++}	10.33	15.61				40.59
Ni^{++}	4.11	6.72				18.40
Pb^{++}	4.51		2.70			7.21
Mn^{++}	10.35				13.36	37.30
NH_4^+	22.71	60.60				83.31
Na^+	25.53			21.10		46.64
K^+	12.51		19.83			32.34

Table 4. Chemicals Used to Prepare Solution B
(Weight in mg to prepare 6 liters)

	mg	mg $SO_4^{=}$	mg NO_3^-	mg F^-	mg Cl^-	mg Reagent
Ca^{++}	150.54				266.32	552.1
Mg^{++}	162.17	640.93				803.1
Zn^{++}	29.86				32.39	62.26
Cd^{++}	29.64				18.69	60.21
Cu^{++}	30.67		59.84			116.6
Ni^{++}	31.11		65.71			154.1
Pb^{++}	31.72		18.98			50.70
Mn^{++}	24.37				31.45	87.79
NH_4^+	147.62	393.91				541.9
Na^+	93.49	195.31				288.8
K^+	30.62				27.76	58.38
Na^+	20.59		55.52			76.12
Na^+	36.91			30.50		67.43

Table 5. Chemicals Used to Prepare Solution C
(Weight in mg to prepare 4 liters)

	mg	mg $SO_4^=$	mg NO_3^-	mg F^-	mg Cl^-	mg Reagent
Ca^{++}	246.15	589.95				836.1
Mg^{++}	145.71				425.09	1219.0
Zn^{++}	61.29		116.25			278.9
Cd^{++}	100.80				63.59	204.8
Cu^{++}	39.88				44.50	107.0
Ni^{++}	101.27	165.70				453.4
Pb^{++}	39.23		23.48			62.71
Mn^{++}	19.96				25.77	71.92
NH_4^+	490.77				966.5	1458.4
Na^+	440.60		1188.23			1629.0
K^+	201.35	247.33				448.7
Na^+	48.50			40.08		88.6

Table 6. Chemicals Used to Prepare Solution D
(Weight in mg to prepare 4 liters)

	mg	mg $SO_4^=$	mg NO_3^-	mg F^-	mg Cl^-	mg Reagent
Ca^{++}	640.8				1133.7	2350.1
Mg^{++}	189.3				552.4	1584.0
Zn^{++}	122.1		231.6			555.6
Cd^{++}	200.7		221.4			550.7
Cu^{++}	80.2		156.6			305.1
Ni^{++}	201.4		425.5			997.9
Pb^{++}	58.8		35.2			93.99
Mn^{++}	40.1				51.8	144.5
NH_4^+	924.3				1821	2747.0
Na^+	597.7	1249.0				1846.9
K^+	611.5	751.1				1362.6
Na^+	410.3		1106.6			1517.1
Na^+	72.8			60.2		133.0

Table 7. Analytical Values for Reconstituted Samples
Sample A

Measured	Synthesis	Analytical Values			Recommended Values*
		Bulk	Ampoules	Diluate	
pH				6.18	6.18
Conductivity**				5.8	5.8
Acidity***		0.49			0.49
$SO_4^=$ (S)	361		342		361
NO_3^- (N)	26	26	26		26
NH_4^+ (N)	89	81	84		89
F^-	102		103		102
Cl^-	106		136		106
Na^+	128	134	153		153
K^+	63	68			63
Ca^{++}	99	96			99
Mg^{++}	104	86			86
Zn^{++}	21	19	20		21
Cd^{++}	26	30			30
Cu^{++}	52	53			52
Ni^{++}	21	23			21
Pb^{++}	23	20	18		18
Mn^{++}	52	55	53		52

* Data believed useful to 2 significant figures

** $\mu S \cdot cm^{-1}$ reconstituted solution

*** mg/l $CaCO_3$

All other units, µg/l reconstituted solution

Table 8. Analytical Values for Reconstituted Samples
Sample B

Measured	Analytical Values					Recommended Values*
	Synthesis	Bulk	Ampoules	Diluate	Acid Rinse	
pH				6.15		6.15
Conductivity**				18.3		18.3
Acidity***		0.50				0.50
$SO_4^=$ (S)	1367		1188			1188
NO_3^- (N)	150	152	150			150
NH_4^+ (N)	382	398	364			382
F^-	102		96			96
Cl^-	1255		1080			1255
Na^+	503	480	516			516
K^+	102	106				102
Ca^{++}	502	442				442
Mg^{++}	541	456				456
Zn^{++}	100	95	94	94^p	96^p	95
Cd^{++}	99	113		116^p	116^p	116
Cu^{++}	102	107		88^p	101^p	88
Ni^{++}	104	109		103^p	104^p	104
Pb^{++}	106	99	92	88^p	104^p	88
Mn^{++}	81	84	83			81

* Data believed useful to 2 significant figures

** $\mu S \cdot cm^{-1}$

*** mg/l $CaCO_3$

All other units, µg/l reconstituted solution

p Polarographic measurement

Table 9. Analytical Values for Reconstituted Samples
Sample C

Measured	Analytical Values: Synthesis	Bulk	Ampoules	Diluate	Acid Rinse	Recommended Values*
pH				6.20		6.20
Conductivity**				59.8		59.8
Acidity***		2.46				2.46
$SO_4^=$ (S)	1672		1645			1672
NO_3^- (N)	1499	1500	1480			1499
NH_4^+ (N)	1909	1890	1858			1909
F^-	200		195			195
Cl^-	7627		7666			7627
Na^+	2446	2420	2460			2460
K^+	1007	1020				1007
Ca^{++}	1231	1216				1231
Mg^{++}	729	722				729
Zn^{++}	307	314	312	309^p	309^p	307
Cd^{++}	500	574		578^p	578^p	578
Cu^{++}	200	198		192^p	198^p	200
Ni^{++}	506	518		506^p	507^p	506
Pb^{++}	196	170	164	152^p	169^p	152
Mn^{++}	100	102	101			100

* Data believed useful to 2 significant figures

** $\mu S \cdot cm^{-1}$

*** mg/l $CaCO_3$

All other units, µg/l reconstituted solution

p Polarographic measurement

Table 10. Analytical Values for Reconstituted Samples
Sample D

Measured	Analytical Values: Synthesis	Bulk	Ampoules	Diluate	Acid Rinse	Recommended Values*
pH				6.07		6.07
Conductivity**				117		117
Acidity***		4.71				4.71
$SO_4^=$ (S)	3333		3374			3333
NO_3^- (N)	2457	2440	2500			2457
NH_4^+ (N)	3595	3590	3524			3595
F^-	301		296			296
Cl^-	17790		16922			17790
Na^+	5404	5260	5444			5444
K^+	3058	3100				3058
Ca^{++}	3204	2840				2840
Mg^{++}	947	922				922
Zn^{++}	610	638	632	610^p	610^p	610
Cd^{++}	1004	1010		1010^p	1010^p	1010
Cu^{++}	401	418		393^p	410^p	393
Ni^{++}	1007	1080		1040^p	1040^p	1007
Pb^{++}	294	125	110	110^p	120^p	110
Mn^{++}	200	204	200			200

* Data believed useful to 2 significant figures

** $\mu S \cdot cm^{-1}$

*** mg/l $CaCO_3$

All other units, µg/l reconstituted solution

p Polarographic measurement